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ANALYSIS OF DEPOSITS FROM BRUCE NGS-A, UNIT 2, BO6

Report No. 91-229-K

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ABSTRACT

A sample of secondary side deposit from Bruce NGS-A, Unit 2, BO6 was analysed. The deposit consisted of flakes, about 600 µm thick, that apparently formed on the tube surfaces. The density of the deposit was 7.4%. and the porosity was about 2 to 5%. The concentrations of major elements present were 52% copper, 23% iron and 9% zinc. These elements were fairly evenly distributed on the cross-section of the flakes, except the concentrations were lowest where silicon was most abundant. The silicon was concentrated on the ID half of the flakes, and the distribution of the silicon indicated the flakes had different origins within the generator.

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36-125-553	836.333	November 6, 1991	91-229-K

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EXECUTIVE SUMMARY

ANALYSIS OF DEPOSITS FROM BRUCE NGS-A, UNIT 2, BO6

P. McSweeney
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Chemical Research Department

A sample of secondary side tube deposit from Bruce NGS-A, Unit 2, BO6 was analysed by physical, chemical, and spectroscopic techniques.

The sample consisted of apparently tube-grown flakes, 360-830 μm thick. the pycnometric density of the deposit was 7.4 g/cm^3. The porosity, determined by image analysis, was about 2-5%.

Major elemental concentrations were 52% copper, 23% iron, and 9% zinc. Most of the copper was present as metallic. About half of the iron was present as either magnetite or substituted spinels, and half as ferric oxides or hydroxides.

Elemental mapping showed that the major elements detected were fairly evenly distributed throughout the cross-section of the flakes, except the concentrations were lowest where silicon was most abundant. Silicon was concentrated on the ID half of the flakes. Possible causes of this silicon distribution are concentration processes during operation and silicon inleakage early in the history of the boiler. The distribution of silicon within the ID half of the flakes indicated the flakes had different origins within the boiler. Manganese appeared to be associated with the presence of silicon in one of the flakes.

P.S.

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36-125-553	836.333	November 6, 1991	91-229-K

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TO: Mr. M.J. Northfield
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ANALYSIS OF DEPOSITS FROM BRUCE NGS-A, UNIT 2, B06

P. McSweeney

1.0 INTRODUCTION

A sample of secondary side tube deposit was recovered from Bruce NGS-A, Unit 2, B06 in December 1989. The sample was obtained during removal of a section of tube from below the first support plate on the centre of the sludge pile, hot side. The sample was submitted to Corrosion Chemistry Section for analysis.

2.0 MACROSCOPIC AND VISUAL

The sample weighed 0.98 g and consisted of seven large flakes, eight small flakes and trace powdered deposit. A photograph of the flakes is shown in Figure 1. The seven large flakes were assigned numbers 1-7 and the eight small flakes were labelled No 8. The flakes were curved in appearance with apparent ID and OD surfaces indicating that they formed on the Inconel 600 tubes. However, some of the deposit labelled No 8 may have been sludge pile particles. At first it was assumed the flakes had formed on the tube that was removed but subsequent analyses indicated that they probably had different origins within the generator.

The flakes were black on the OD surfaces but the ID surfaces varied grey, brown and black. The thickness of the seven large flakes, measured with a Mitotayo digital micrometer, was 510-830 µm. The eight small flakes were 360-520 µm thick.

Flakes No 1, 3, 4 and 7 were sent to B&W Alliance for use in the Bruce NGS-A chemical cleaning solvent development program. However, these flakes were used for density and X-ray fluorescence analyses before they were sent.

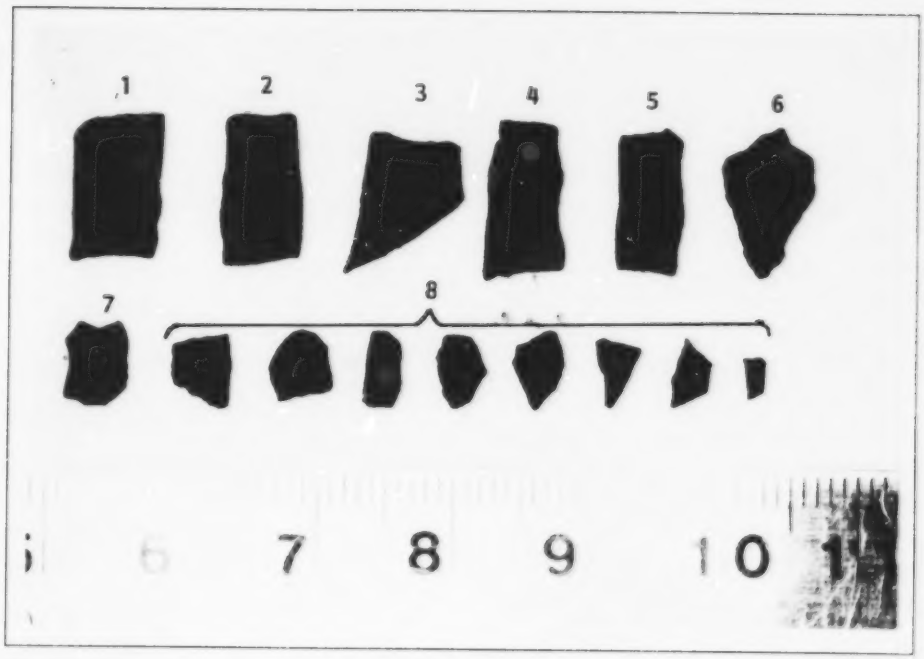


FIGURE 1

MACROGRAPH OF DEPOSIT

3.0 DENSITY AND POROSITY

The average density of a sample consisting of six of the large flakes was determined by pycnometry using acetone as the pycnometric fluid. The density was 7.4 g/cm^3. The high density suggests the presence of a substantial concentration of copper, which tends to occur in metallic form in boiler deposits, yielding a dense structure. For comparison, densities of 4.3-5.8 g/cm^3 were obtained for three samples of Bruce NGS-A Unit 2 boiler deposits in 1982/1/.

The porosity of flakes No 2, 5 and 6 was determined at Ecole Polytechnique de Montreal using an IBAS interactive image analysis system coupled to a Zeiss optical microscope. The flakes were mounted in epoxy resin and a cross-section polished to 1 μm. The volume fraction porosity of the polished surfaces was determined by thresholding the image to isolate the porosity. Several fields bordering the ID and OD edges were examined on each flake. The fields were about 250 μm diameter.

The results are shown in Table 1. The average porosity was 2.2 - 5.1%. In flake No 2, the porosity of the OD half of the flake was consistently greater than that of the ID half. The low porosities are consistent with the high density observed for this deposit.

TABLE 1
POROSITY OF FLAKES

Flake No	2		5		6	
Location of Field	Near ID	Near OD	Near ID	Near OD	Near ID	Near OD
Porosity (%)	2.0 2.0 2.7	4.3 3.3 4.3	2.9 6.4 4.5 2.9 2.1	5.1 6.1 3.7 3.7 4.2	4.7 4.8 4.3 9.9 1.6	3.0 3.2 5.4 4.1 3.0
Aver. Porosity (%)	2.2	4.0	3.8	4.6	5.1	3.7

4.0 X-RAY DIFFRACTION AND X-RAY FLUORESCENCE

Crystalline phase analysis was performed on flakes No 5 and 8 using X-ray diffraction. The flakes were pulverized and pelletized prior to analysis.

Metallic copper and magnetite (Fe_3O_4) were the major phases detected on both flakes. Spinels ($Fe_{3-x}M_xO_4$) may also have been present but XRD analysis can not discriminate many spinels such as those containing zinc and nickel. Tenorite (CuO) and cuprite (Cu_2O) were minor phases. Other crystalline phases were not detected.

X-ray fluorescence analysis was performed on both the ID and OD surfaces of seven flakes. This technique detects elements having atomic number greater than 11. The technique is not very surface-sensitive. Because the flakes were relatively thin, X-rays may have penetrated right through allowing detection of heavy elements on the opposite surface such as copper and iron.

Table 2 shows the results for flake No 1 which exhibited typical elements and orders of abundance. The complete X-ray fluorescence results are given in Appendix 1. The elements are reported in relative order of abundance subject to the judgment of the analyst. Copper was the most abundant element on all surfaces, except on two OD surfaces where zinc was more abundant. Iron and zinc were next in abundance on most surfaces - iron on the ID surface and zinc on the OD.

TABLE 2
ELEMENTS DETECTED BY X-RAY
FLUORESCENCE ANALYSIS OF FLAKE NO 1

ID Surface	OD Surface
Cu	Cu
Fe	Zn
Zn	Fe
Ni	Ca
Sn	Si
Mn	Ni
Mo	Mn
Cr	Al
Si	Cr
	Mg

5.0 MOSSBAUER SPECTROSCOPY

Flakes No 5 and 8 were analyzed at Chalk River Laboratories using ^{57}Fe Mossbauer spectroscopy in a transmission geometry, at a temperature of 273K, to identify iron oxide phases.

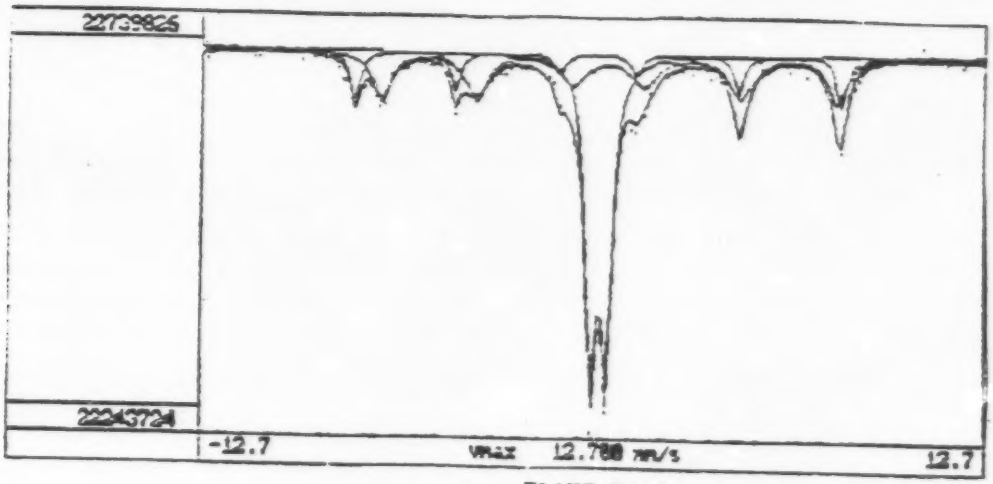
The spectra obtained are shown in Figure 2 and the results are shown in Table 3.

TABLE 3
RESULTS OF MOSSBAUER SPECTROSCOPY ANALYSIS

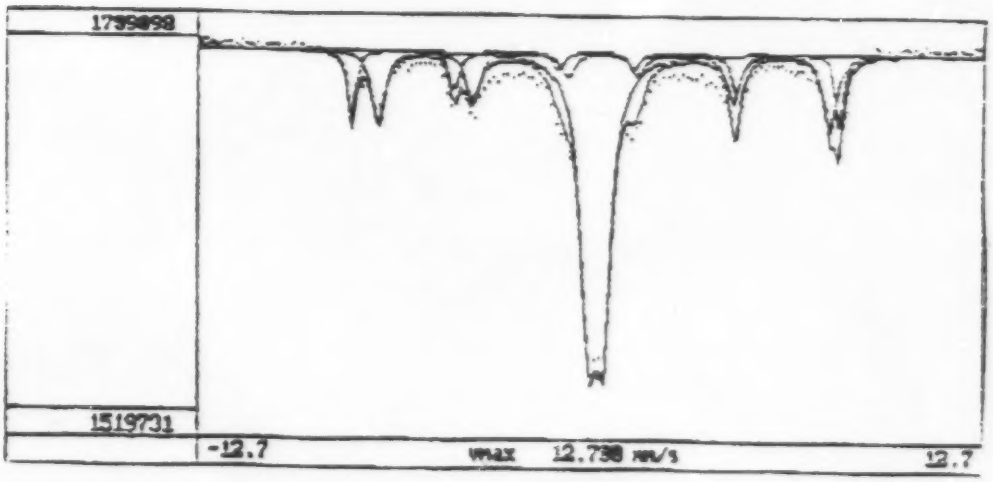
	Fe Present as Fe_3O_4 or Spinel	Fe Present as Ferric Oxides or Hydroxides
Flake No 5	53.4%	46.6%
Flake No 8	43.4%	56.6%

Of the iron present, 43-53% consisted of magnetite or substituted spinels ($Fe_{3-x}M_xO_4$). The remainder was present as ferric oxides or hydroxides such as lepidocrocite (γ-FeOOH). Because XRD did not detect these ferric compounds they are assumed to have been present in amorphous form. An attempt was made to analyze the samples at a temperature of 4K to obtain more information on spinels, but because of equipment failure and time constraints the analyses were not completed.

Iron oxide accumulations in nuclear boilers are generally called magnetite, leading to the misconception that all or most of the iron is present as Fe_3O_4. The Mossbauer results indicate that half the iron in the sample was present as ferric oxides or hydroxides. Further, some or all of the magnetite-type iron may be present as complex spinels containing zinc, nickel and other metals substituting for iron.



FLAKE NO 5



FLAKES NO 8

FIGURE 2: MOSSBAUER SPECTRA FOR FLAKES NO 5 AND 8

6.0 ELEMENTAL

Elemental analysis was performed on the flakes comprising No 8. The deposit was solubilized by wet-ashing with aqua regia and hydrofluoric acid and analyzed by inductively coupled plasma emission spectroscopy (ICP). Because deposit No 8 consisted of several small flakes it was considered more representative of bulk steam generator deposits than an individual large flake. Elemental analysis of flake No 5 had been planned but the amount of deposit remaining after performing other analyses was not sufficient to yield reliable results.

The analytic results are shown in Table 4. The deposit contained about 52% copper. While boiler deposits normally contain less copper than this, material lanced from a Bruce Unit 2 boiler in 1989 contained copper concentrations as high as 70%/2/. The concentration of zinc was also higher than what normally occurs in deposits. No lead, a possible source of corrosion of Inconel 600, was detected. The mass balance from the analyses was excellent: assuming metals other than copper were present as oxides, there was excellent recovery of the mass of deposit analysed.

TABLE 4
ELEMENTAL ANALYSIS OF DEPOSIT NO 8

	Concentration - g/kg
Cu	516
Fe	234
Zn	92.8
Ni	19.6
Mn	19.6
Al	2.7
Si	1.7
Cr	0.92
P	0.69
Mg	0.51
S	0.31
Ti	0.31
Pb	<0.2
Mo	0.17
Ca	0.14
Na	0.096
K	0.044
Total	890

7.0 X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopy (XPS) was employed to study the oxidation states of copper and sulfur on the ID and OD surfaces of flakes No 2, 5 and 6. XPS is a surface sensitive technique that detects elements to a depth of 3-5 nm. Spectral areas were about 500 μm in diameter.

The concentration of carbon on the surfaces was high due, apparently, to atmospheric contamination. No sulfur was detected on any of the flakes. Despite the high copper content of the deposits, no metallic copper was detected on the surface. Oxidized copper was detected but the concentration was too low to identify the oxidation state.

In an attempt to remove surface contamination, flake No 2 was rinsed in dichloromethane and ethanol. Because this did not significantly reduce the concentration of carbon, the flake was treated with ozone and ultraviolet radiation under vacuum to oxidize and remove organic carbon. This treatment removed most of the carbon; however, it is not known whether it altered the oxidation states of copper and sulfur. Figure 3 shows the spectrum of the ID surface of flake No 2 after the ozone and ultraviolet radiation treatment. Binding energies indicated the presence of tenorite (CuO) and possibly cuprite (Cu_2O). The surface contained 0.5% sulfur present as either $SO^{=}_4$ or $SO^{=}_3$, and 0.4% sulfur present as other species, possibly sulfide.

8.0 SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDX)

A scanning electron microscope with EDX capability was used to survey elements with atomic number >11, representing surface material to a depth of about 1 μm. EDX was employed to determine relative elemental composition and SEM provided elemental mapping of the surfaces.

The relative composition of the ID and OD surfaces of flakes No 2 and 5 was determined on spectral areas 300 μm across. The results are presented in Table 5. Except for the OD of flake No 2, the concentration of copper was substantially lower than what was observed by ICP analysis of flakes No 8 (Table 4).

TABLE 5
RELATIVE COMPOSITION OF FLAKE SURFACES BY SEM

Flake No and Surface	Element Concentration - (Wt. %)									
	Fe	Cu	Ni	Zn	Mg	Al	Si	Ca	Cr	Mn
No 2, OD	36.7	50.0	3.5	9.8	*					
No 5, OD	40.9	25.8	4.7	23.3		3.0	1.2	0.2		1.1
No 2, ID	19.2	11.8	2.0	21.1	5.3	4.5	7.0	24.2		4.9
No 5, ID	19.8	39.5	3.2	21.5	3.3	4.3	6.3	0.2	0.3	1.6

* Vacant space indicates element not detected.

To obtain information on cross-sections, flakes No 2, 5 and 6 were mounted in epoxy resin and polished to 1 μm grit. Average surface composition was determined by scanning a region that encompassed the entire diameter of the flake. Table 6 shows the results obtained. The concentrations of aluminum and silicon were substantially higher than what was observed by ICP analysis of flakes 8 (Table 4). The mounting resin - a possible source of contamination, was checked for the presence of aluminum and silicon by SEM but chlorine was the only element detected. However, bulk chemical analyses and surface sensitive analyses frequently disagree.

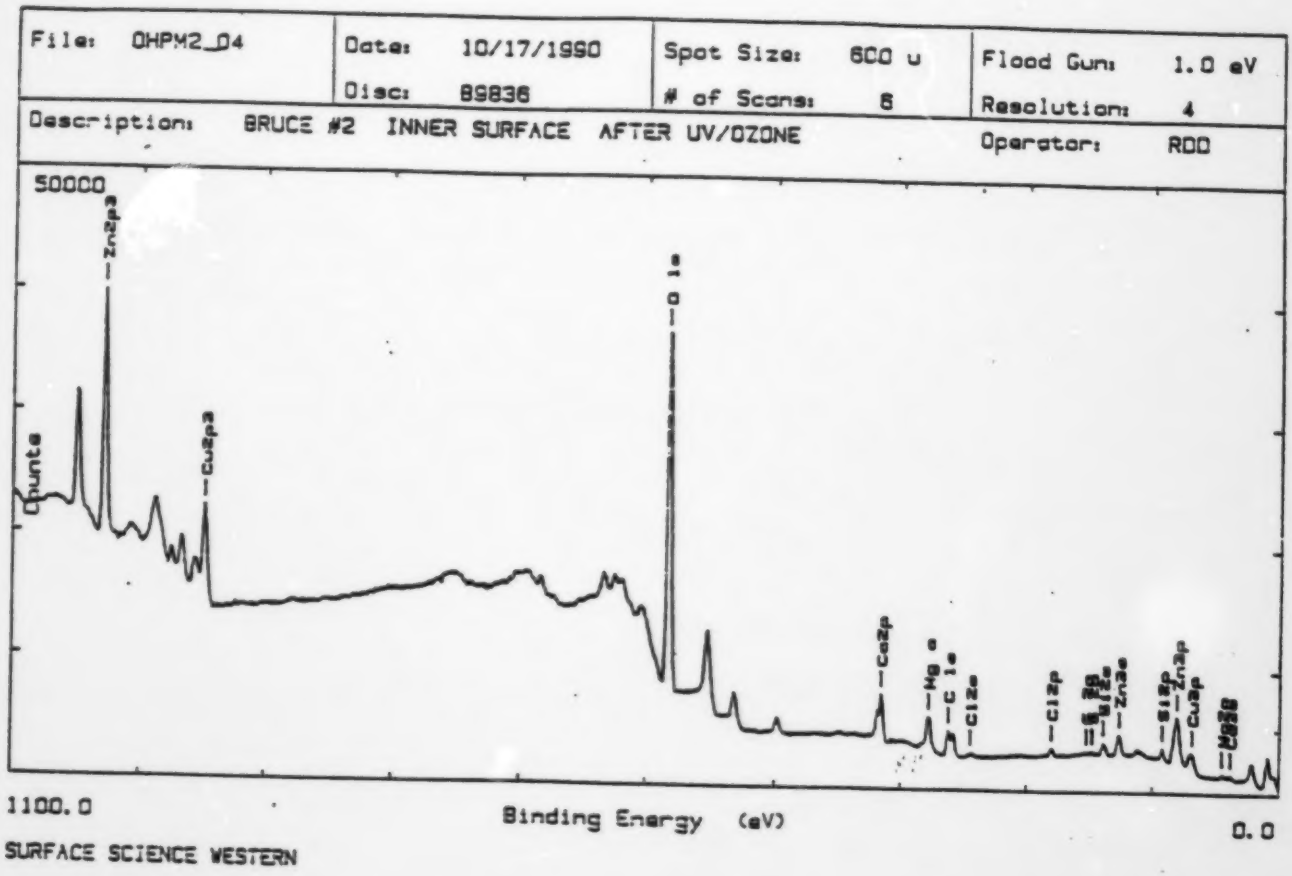


FIGURE 3: XPS SPECTRUM OF FLAKE NO 2 AFTER OZONE/UV TREATMENT

TABLE 6
RELATIVE COMPOSITION OF POLISHED SURFACES BY SEM

	Relative Composition (Wt. %)		
	Flake No 2	Flake No 5	Flake No 6
Fe	29.9	21.8	24.1
Cu	33.4	24.1	21.3
Ni	2.6	1.9	1.9
Zn	14.6	15.0	7.4
Cr	0.3	0.5	0.9
Al	16.1	14.6	10.3
Si	2.0	12.0	13.3
Mg	*	7.9	17.3
Mn	0.4	1.0	0.7
P		0.9	1.6
S	0.7	0.4	1.3

* Vacant space indicates element not detected.

Elemental mapping of the polished surfaces was performed by EDX. The results are presented in Figures 4 through 6. Each table shows an SEM micrograph of the area to be mapped followed by the elemental maps.

Iron, copper, zinc and nickel, the major metals present, were fairly evenly distributed, except that concentrations were lowest where silicon was most abundant. Most of the silicon was concentrated on the ID half of the flakes; possible causes of this are concentration processes during operation and silicon inleakage early in the history of the boiler. The distribution of silicon within the ID half of the flakes indicates that the flakes did not have the same origin. For example, flake No 5 contained a silicon-rich layer 40 µm thick at the ID surface. Spot mode analysis of dark regions on the SEM micrograph of flake No 6, ID half, confirmed the regions were rich in silicon. The sharp demarcation in the centre of flake No 6 was associated with the distribution of silicon, and with a difference in morphology as shown in the SEM micrograph. Aluminum appeared to be abundant at the demarcation. Manganese was associated with the presence of silicon in flake No 2.

9.0 CONCLUSIONS

A sample of secondary side deposit from Bruce NGS-A, Unit 2, B06 was analysed by physical, chemical and spectroscopic techniques.

The sample consisted of apparently tube-grown flakes, 360-830 um thick.

The density of the deposit was 7.4 g/cm^3. The porosity, as determined by image analysis, was 2.2 - 5.1%.

The concentrations of major elements were 51.6% Cu, 23.4% Fe and 9.3% Zn. Major crystalline phases detected were metallic copper and magnetite.

Mossbauer spectroscopy analysis showed that about half of the iron was present as Fe_3O_4 or substituted spinel, while the remainder was present as ferric oxides or hydroxides. Elemental mapping of the polished surfaces of three flakes showed fairly even distribution of the major metals - iron, copper, zinc, except that concentrations were lowest where silicon was most abundant. Silicon was concentrated on the ID half of the flakes suggesting either a concentration process during operation or silicon inleakage early in the history of the generator. The distribution of silicon suggested the flakes had different origins within the generator. Manganese appeared to be associated with the presence of silicon in one flake.

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10.0 REFERENCES

1. Gonzalez, F., "Analysis of Bruce NGS Steam Generator Deposits", Research Division Report 82-198-K.

2. Eatock, J.W., "Bruce NGS-A Unit 2 Boiler Deposit Inventory R-1", CPSD Memorandum PCP-12603.1, January 31, 1990

APPENDIX 1

ELEMENTS DETECTED BY X-RAY FLUORESCENCE SPECTROSCOPY

FLAKE #1

ID SURFACE	OD SURFACE
Cu	Cu
Fe	Zn
Zn	Fe
Ni	Ca
Sn	Si
Mn	Ni
Mo	Mn
Cr	Al
Si	Cr
	Mg

FLAKE #2

ID SURFACE	OD SURFACE
Cu	Zn
Fe	Cu
Zn	Fe
Ni	Ca
Sn	Si
Mn	Ni
Cr	Mn
Mo	Al
	Sn
	Cr

FLAKE #3

ID SURFACE	OD SURFACE
Cu	Cu
Fe	Zn
Zn	Fe
Ni	Si
Ca	Ni
Sn	Ca
Mo	Mn
Mn	Al
Si	Mg
Cr	Mo

FLAKE #4

ID SURFACE	OD SURFACE
Cu	Zn
Fe	Cu
Zn	Fe
Ni	Mn
Sn	Si
Mo	Ni
Mn	Ca
Cr	Al
	Mg
	Mo
	Cr

FLAKE #5

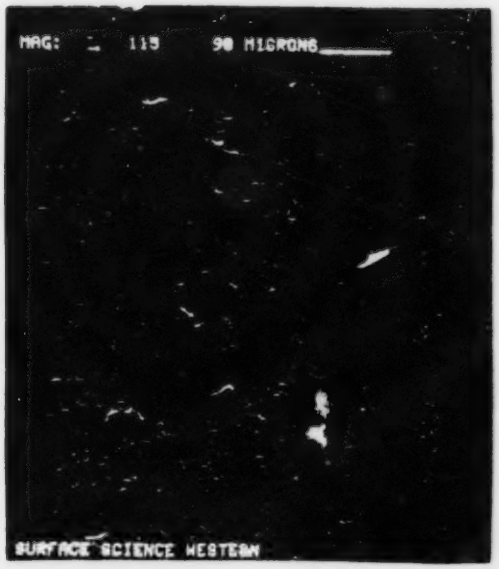
ID SURFACE	OD SURFACE
Cu	Cu
Fe	Zn
Zn	Fe
Ni	Si
Sn	Ni
Mo	Mn
Mn	Ca
Cr	P
	Sn
	Mo
	Cr

FLAKE #6

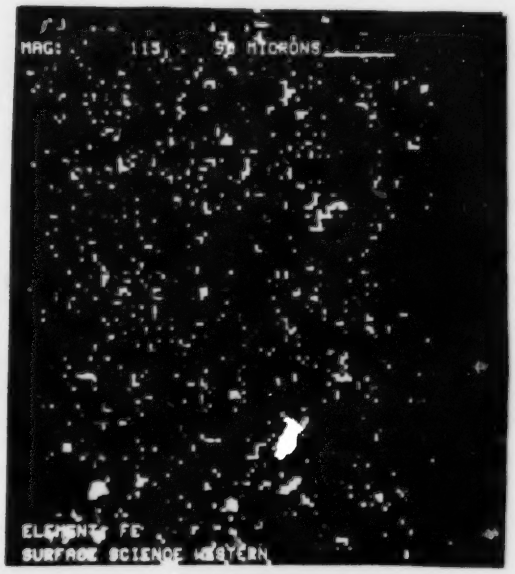
ID SURFACE	OD SURFACE
Cu	Cu
Fe	Fe
Zn	Zn
Ni	Ni
Ca	Ca
Mn	Si
Si	P
Sn	Mn
P	Al
Al	Sn
Cr	Mo
Mo	Cr

FLAKE #7

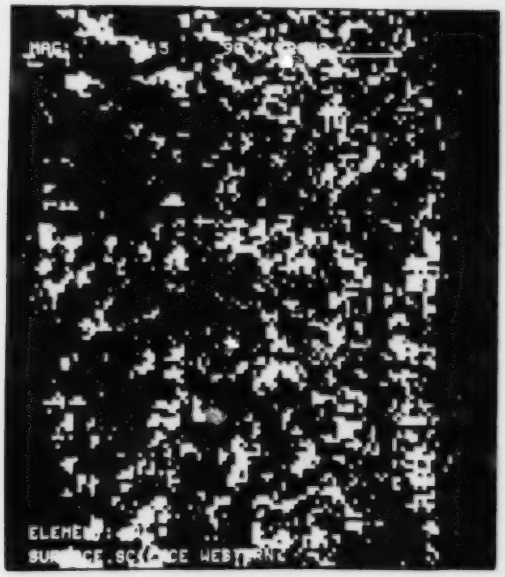
ID SURFACE	OD SURFACE
Cu	Cu
Zn	Zn
Fe	Fe
Ca	Ni
Mn	Si
Ni	Ca
Mo	P
Sn	Mn
Cr	Al
	Sn
	Cr
	Mo



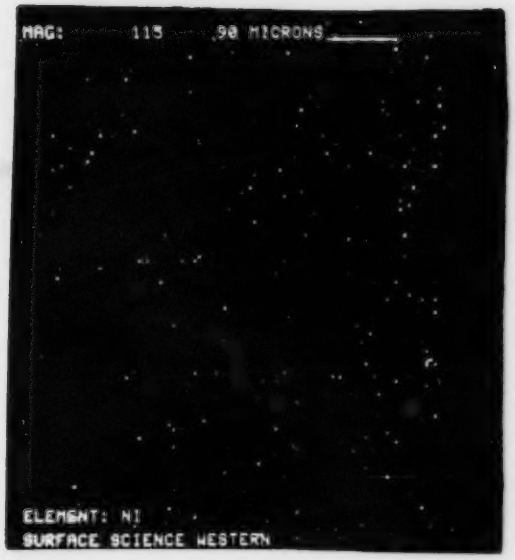
SEM Micrograph



Fe Map



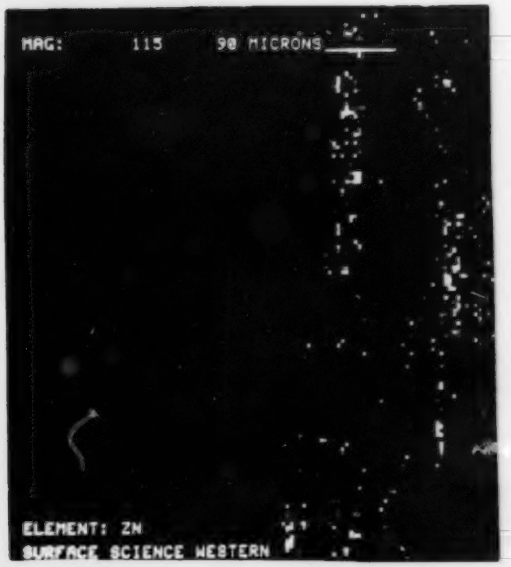
Cu Map



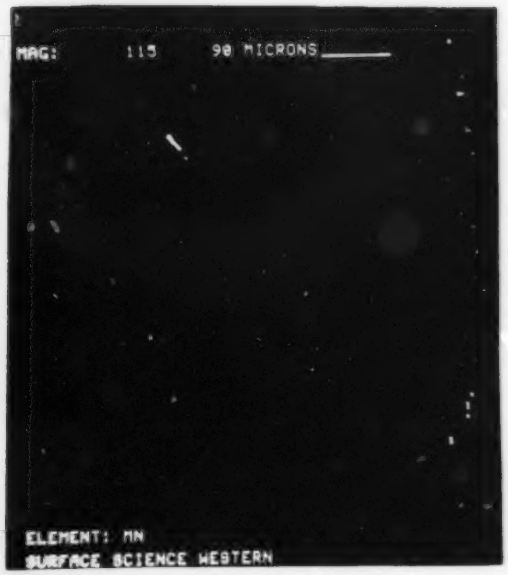
Ni Map

FIGURE 4

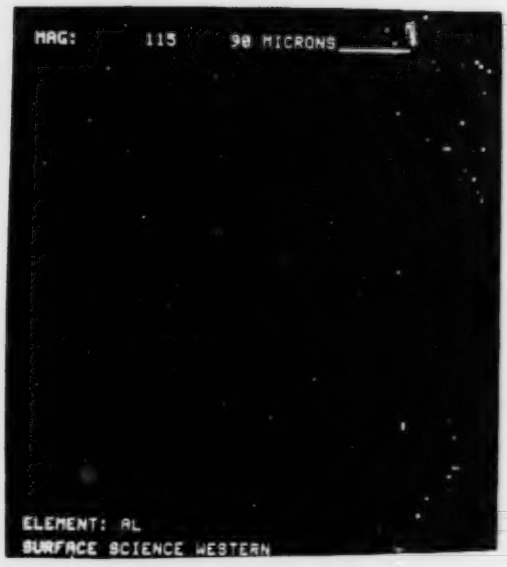
SEM MICROGRAPH AND EDX MAPS OF FLAKE NO. 2
(Right margins represent ID edge of flake)



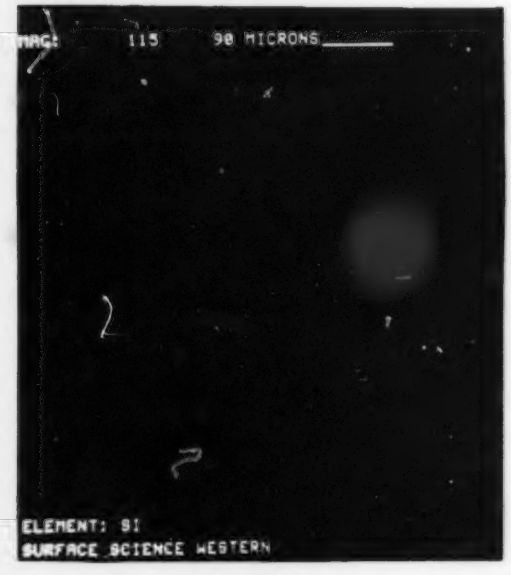
Zn Map



Mn Map



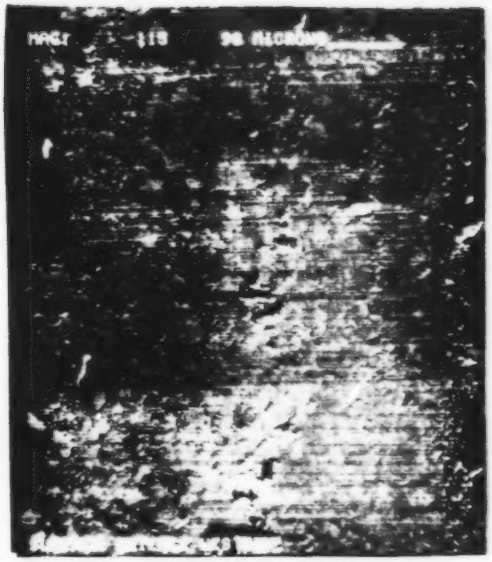
Al Map



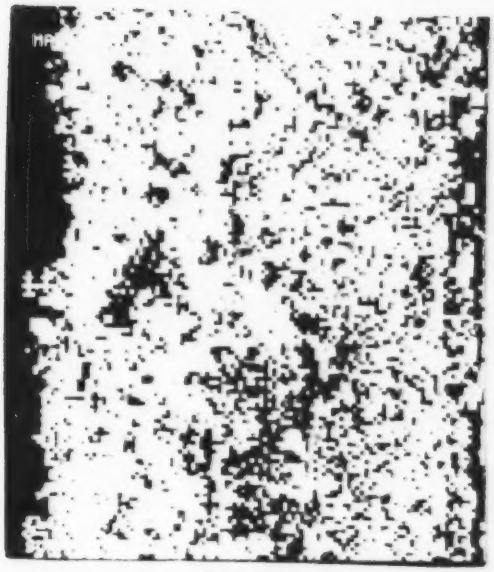
Si Map

FIGURE 4 CONTINUED

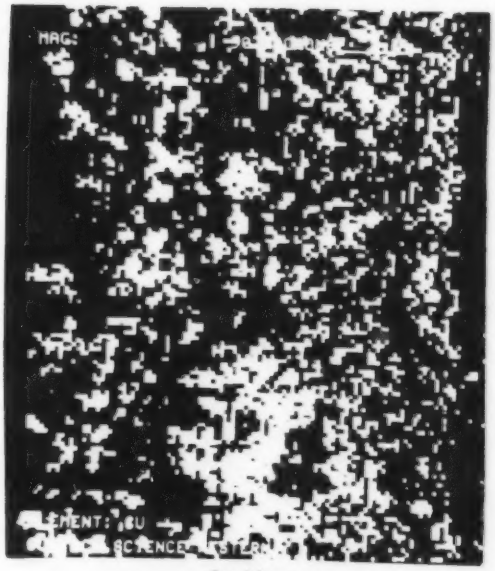
(FLAKE NO. 2)



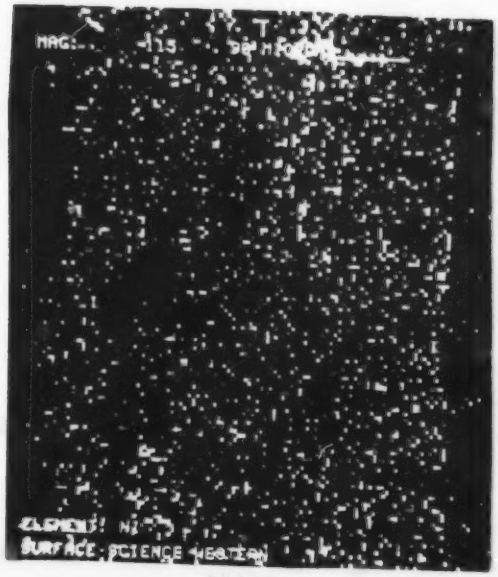
SEM Micrograph



Fe Map



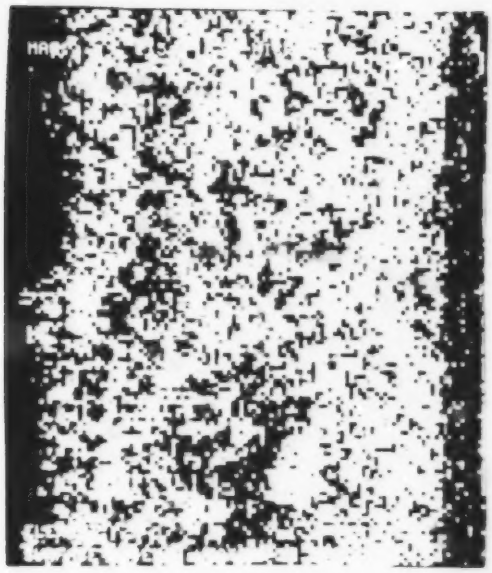
Cu Map



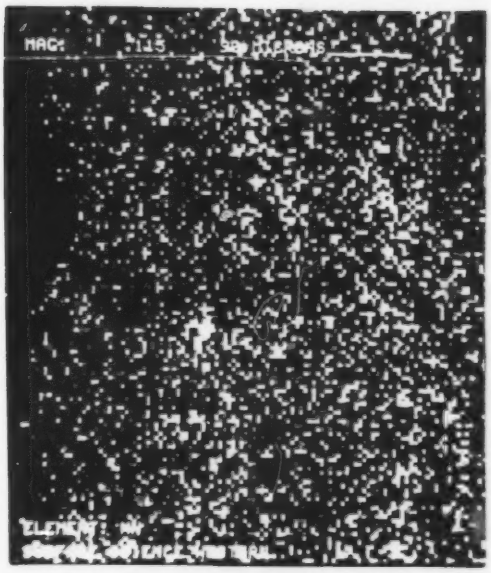
Ni Map

FIGURE 5

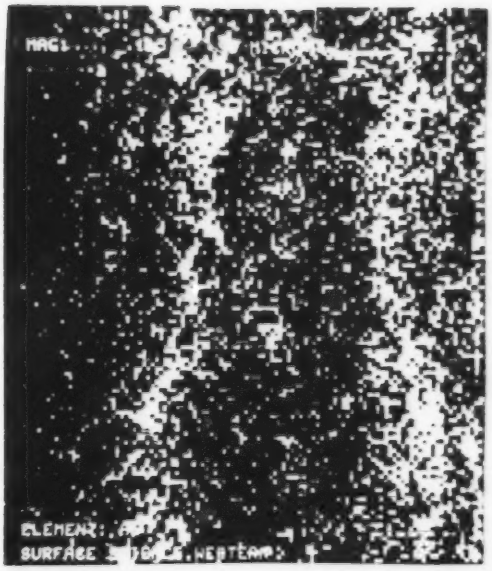
SEM MICROGRAPH AND EDX MAPS OF FLAKE NO. 5
(Right margins represent ID edge of flake)



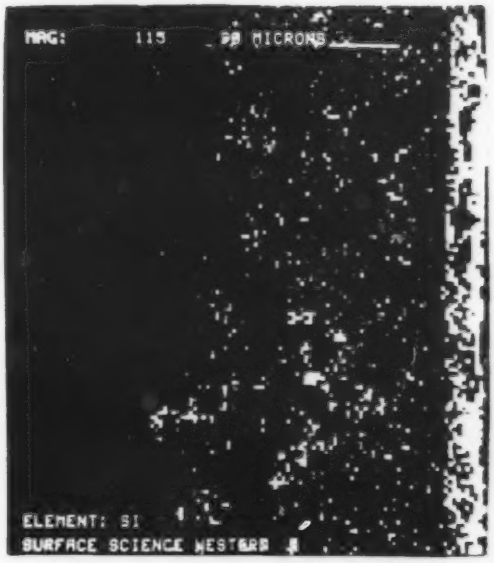
Zn Map



Mn Map



Al Map

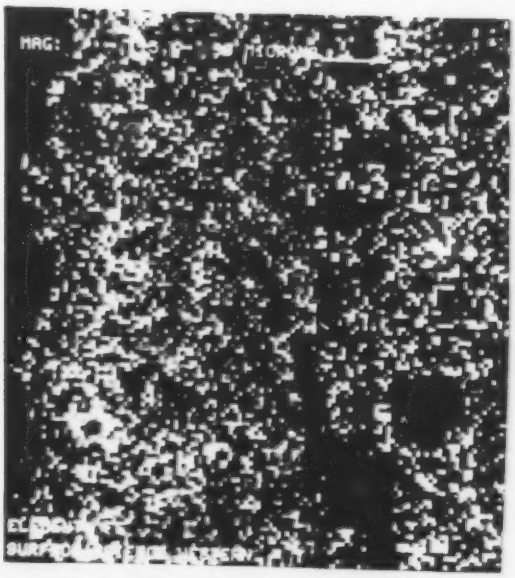


Si Map

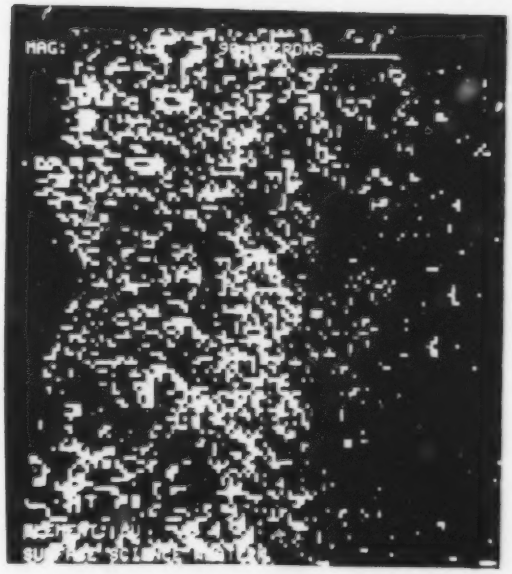
FIGURE 5 CONTINUED

(FLAKE NO. 5)

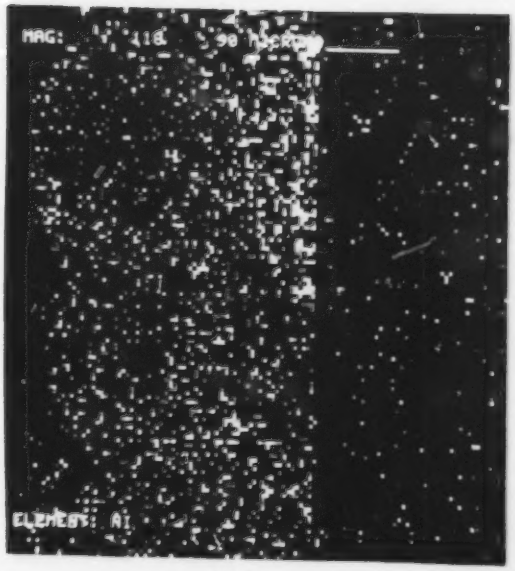
SEM Micrograph



Fe Map



Cu Map



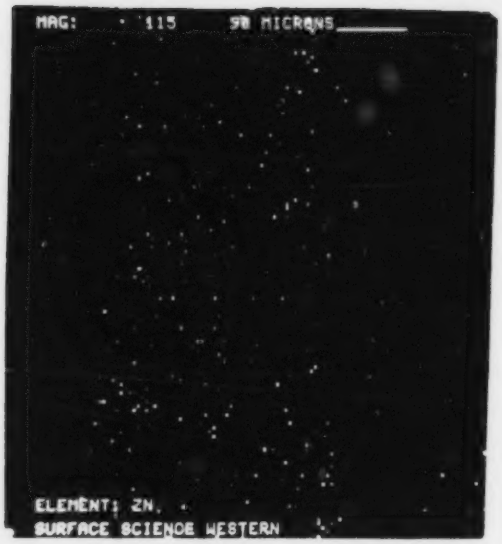
Ni Map

FIGURE 6

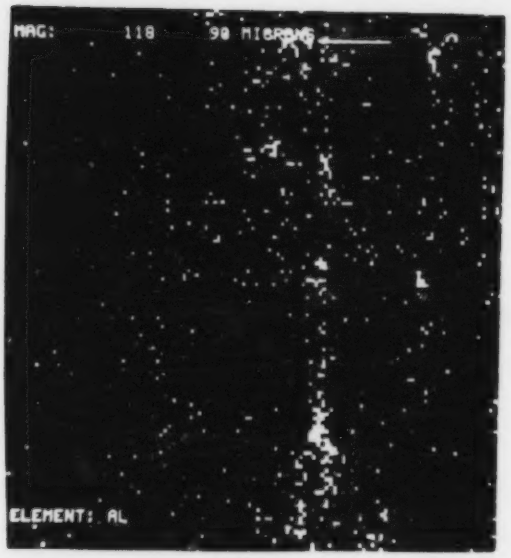
SEM MICROGRAPH AND EDX MAPS OF FLAKE NO. 6
(Right margins, represent ID edge of flake)

91-229

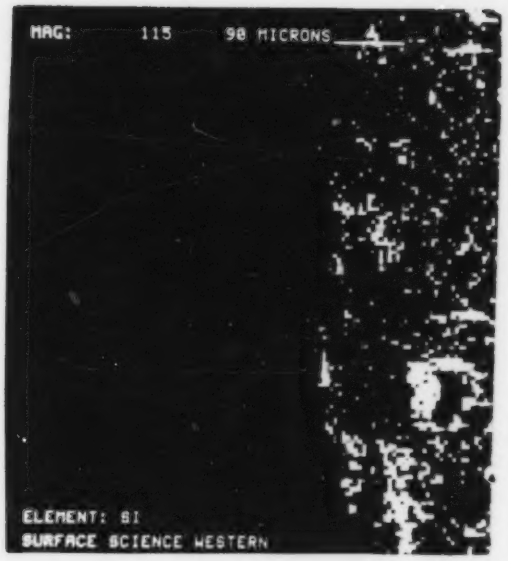
186373-839-RD



Zn Map



Al Map



Si Map

FIGURE 6 CONTINUED

(FLAKE NO. 6)